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Arene non-innocence in dinuclear complexes of Fe, Co, and Ni supported by a *para*-terphenyl diphosphine†

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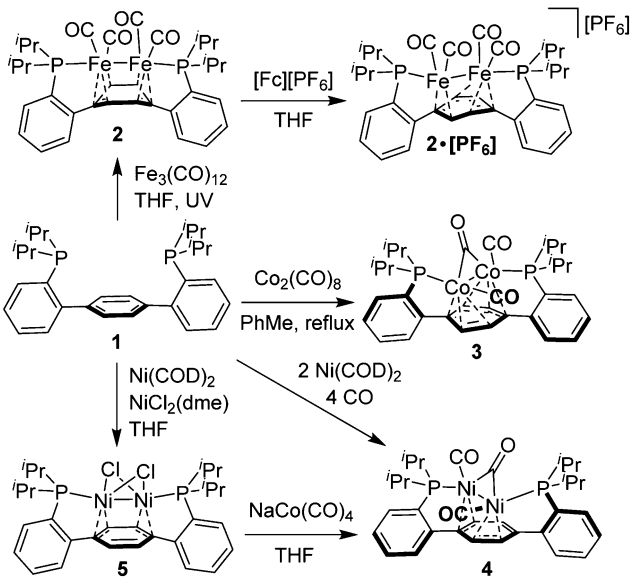
Cofacial Fe_2, Co_2, and Ni_2 complexes supported by a *para*-terphenyl diphosphine ligand were prepared. Central arene deplanarization and a μ_2:(η^3,η^3) coordination mode suggest partial bisallyl character in the Fe_2 and Co_2 complexes. An oxidation induced shift in Fe_2–arene binding highlights the non-innocent nature of the arene ligand.

Dinuclear metal complexes have the potential to act in a cooperative fashion in small molecule activation and multi-electron processes.[1] In particular, low-valent Fe_2, Co_2, and Ni_2 complexes have been shown to participate in a variety of transformations, including proton reduction,[1a–c] dihydrogen activation,[1d] Pauson–Khand-type cycloadditions,[1e] C–C coupling,[1f–h] group transfer,[1i,j] and carbon dioxide activation.[1k–n] The development of novel dinucleating ligand scaffolds and complexes capable of both undergoing redox processes and facilitating novel chemical transformations is currently a topic of active research.[2] Our group has recently utilized bis- and tris(phosphinoaryl)benzene ligands as multinucleating scaffolds for Ni and Pd complexes, where the central arene participates as a flexible donor ligand.[1g,3] Herein, we describe a series of dinuclear, first-row transition metal complexes supported by a *para*-terphenyl diphosphine, compound **1** (Scheme 1), and the changes in Fe_2–arene coordination upon one-electron redox chemistry.

After multiple days of ultraviolet irradiation, a tetrahydrofuran (THF) solution of compound **1** and $Fe_3(CO)_{12}$ yielded a Fe_2 complex, **2**, in 11% isolated yield (Scheme 1). Refluxing a toluene (PhMe) solution of compound **1** and $Co_2(CO)_8$ at 110 °C overnight cleanly afforded a Co_2 complex, **3**, in 54% isolated yield (Scheme 1). The analogous cofacial Ni_2 complex was prepared by the reduction of a previously synthesized Ni^I–Ni^I dichloride complex, **5**,[1g] with Na[Co(CO)$_4$], which served as a source of both reducing equivalents and carbon monoxide (CO) ligands. The Ni_2 complex, **4**, was isolated in 11% yield (Scheme 1). An alternative



Scheme 1 Synthesis of dinuclear Fe, Co, and Ni carbonyl complexes.

synthesis of complex **4** involved the addition of four equivalents of CO to two equivalents of Ni(COD)$_2$ (COD = 1,5-cyclooctadiene) and compound **1** (Scheme 1). However, this method was lower yielding and not used as the primary synthetic route. The low yields for compounds **2** and **4** are due to purification procedures, which require isolation of crystalline material. The reaction mixtures for the syntheses of these complexes display the desired compounds as the major species by ^{31}P NMR spectroscopy.

Single crystal X-ray diffraction (XRD) studies of complexes **2**, **3**, and **4** confirmed the stabilization of dinuclear fragments by metal–arene interactions (Fig. 1). The dinuclear core of complex **2** and **3** coordinate in a μ_2:(η^3,η^3) fashion to the central arene. In **2**, the phosphines coordinate roughly along the Fe–Fe vector, resulting in a structure of *pseudo*-C_{2v} symmetry. The zig-zag arrangement of the P_2Co_2 moiety in **3**, imposed by the bridging and terminal CO ligands on Co, effects the overall *pseudo*-C_2 symmetry of the dicobalt complex. In complex **2**, the planes

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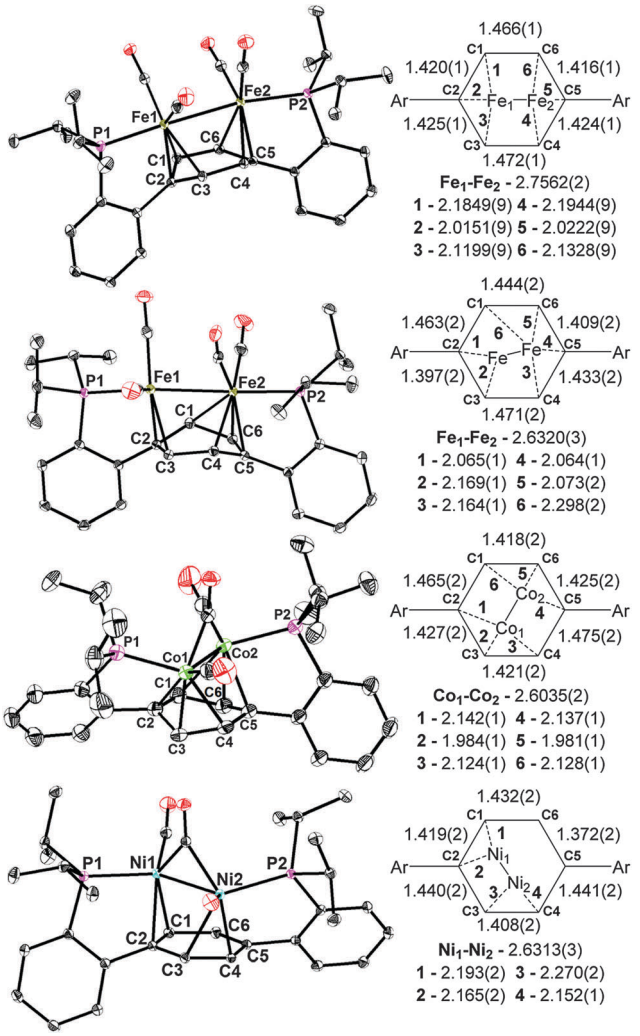

Fig. 1 Solid-state structures as 50% thermal ellipsoids of complexes (from top to bottom) **2**, **2**·[PF_6], **3**, and **4**. Hydrogen atoms, solvents, and counteranions have been omitted for clarity. Selected bond distances for each complex are shown on right.

defined by C1–C2–C3 and C4–C5–C6 show an average dihedral angle of 26° with the C1–C3–C4–C6 plane. Central arene deplanarization is also observed in complex **3**, with a dihedral angle of averaging approximately 23° between both the C2–C3–C4 and C5–C6–C1 planes with the C1–C2–C4–C5 plane. The deplanarized central arene carbons of complex **3** are *ortho* to the aryl substituents, oriented to match the Co–Co vector. The C–C bonds separating the η^3-M moieties are considerably elongated, averaging approximately 1.469 Å for C1–C6 and C3–C4 in complex **2** and 1.470 Å for C1–C2 and C4–C5 in complex **3**. These structural features are consistent with reduction of the arene to generate a bisallyl motif and formal oxidation of the M_2 core by two electrons to yield a M^I–M^I unit (M = Fe, Co). Further supporting this assignment are short M–arene distances that are consistent with literature bisallyl Fe_2 or Co_2 complexes.[4] Bridging arene complexes of Fe_2 and Co_2 displaying a bisallyl motif are very rare and typically have the two metal centers bound in transfacial manner.[5,6] Compounds **2** and **3** represent unusual examples of cofacially coordinated μ_2-arene complexes. The Fe–Fe distance in complex **2** (2.7563(2) Å) is comparable to a cofacial μ_2:(η^3,η^3)-toluene Fe_2 complex at 2.746(1) Å,[5b] but shorter than typical bisallyl diiron compounds which range between 2.927(3) and 3.138(3) Å.[4b–d] The Co–Co distance (2.6035(2) Å) in **3** is in the range for a formal single Co^0–Co^0 bond.[7]

In contrast to the Fe_2 and Co_2 systems, the Ni_2 core of **5** binds μ_2:(η^2,η^2) to adjacent C–C bonds of the central arene. In the solid-state, **4** shows partial localization of single bond character at C1–C6, C2–C3, and C4–C5 indicative of disrupted aromaticity. No deplanarization of the central arene ligand is observed, suggesting that bisallyl character is not present. While transfacial μ_2:(η^2,η^2)-arene Ni^0Ni^0 complexes are known,[8] **4** displays the first structurally characterized cofacial μ_2:(η^2,η^2) binding mode. The coordination sphere of Ni in **4** is reminiscent of $Ni_2(CO)_3(dppm)_2$ with a phosphine donor replaced by an arene double bond for each metal center (dppm = bis(diphenyphosphino)methane).[10a]

The ^{1}H NMR chemical shifts of the central arene protons of complex **2**, **3**, and **4** are shifted upfield in comparison to the parent ligand, as a singlet at 4.39 ppm, a pair of 1 : 1 singlets at 4.29 and 3.95 ppm, and a singlet at 5.85 ppm, respectively, indicating that strong metal–arene interactions and disruption of aromaticity are preserved in solution. The NMR spectra of **2** are consistent with the high symmetry observed in the solid-state structure. Variable temperature (VT) ^{1}H NMR experiments with **3** show broadening of the central arene and methine protons upon heating, with coalescence observed around 80 °C (Fig. S11, ESI†). The fluxional process consistent with the observed NMR features involves the interconversion of the two *pseudo*-C_2 isomers by partial rotation of the Co_2 unit around the central arene ring. VT ^{1}H NMR studies with complex **4** show decoalescence of the central arene protons into a pair of doublets at −20 °C (Fig. S12, ESI†). Further cooling to −78 °C was not sufficient to resolve the central arene protons into four separate resonances indicating the complex was not locked out as the C_1 solid-state structure due to partial rotation of Ni_2-unit. In agreement, the ^{31}P NMR spectrum shows a single peak, even at −78 °C. The lower energetic barrier for the fluxional process in **4** *versus* **3** may be due to a smaller molecular distortion, particularly of the central ring, necessary for partial rotation of the M_2 unit of **4**.

The IR spectrum of complex **2** displays peaks corresponding to terminal CO stretches at 1966, 1914, 1903, and 1880 cm^{-1}. This is comparable to an asymmetrically substituted [FeFe]-hydrogenase model complex, (μ-pdt)[$Fe^I(CO)_2(PMe_3)$][$Fe^I(CO)_2$(IMes)] (pdt = 1,3-propanedithiolate, IMes = 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene), with CO stretches at 1972, 1933, 1897, and 1882 cm^{-1}.[9] Complex **3** shows peaks consistent with the presence of two terminal (1946 and 1928 cm^{-1}) and one bridging (1771 cm^{-1}) CO ligands, as observed in the solid-state.[10] Similarly, complex **4** shows IR absorptions for two terminal (1972, 1952 cm^{-1}) and one bridging (1803 cm^{-1}) CO ligands.[10]

Cyclic voltammetry (CV) studies of complex **2** revealed a quasireversible oxidation at −0.44 V *versus* the ferrocene (Fc) and ferrocenium couple (Fig. S13, ESI†). Complexes **3** and **4** did not show reversible redox events in CV studies, and chemical oxidations led to decomposition. The addition of one equivalent of [Fc][PF_6] to a THF solution of complex **2** resulted in a color

change from orange-red to green. The one-electron oxidized complex, **2**·[PF_6], was isolated in 41% yield, but was found to be unstable in solution at ambient temperatures. However, crystals of complex **2**·[PF_6] grown at −35 °C are stable for weeks in the solid-state and proved suitable for XRD analysis.

Oxidation of complex **2** results in significant structural changes to both the coordination mode of the Fe_2 core to the central arene and the nature of the central arene deplanarization (Fig. 1). The diiron core binds in an μ_2:(η^2,η^4) fashion, consistent with a distorted neutral ene-diene assignment for the arene. The longest C–C distances are C1–C2 and C3–C4 (average of 1.467 Å), which correspond to the bonds separating the metal-bound olefin and diene fragments. This is an unusual structural motif for an arene coordinated to a dinuclear unit. The Fe–Fe bond of **2**·[PF_6] has contracted to 2.6320(3) Å, over 0.12 Å shorter than the Fe–Fe bond of complex **2**, suggestive of a strengthened metal–metal bonding interaction. The IR spectrum of **2**·[PF_6] shows peaks at 2010, 1972, 1938, and 1917 cm^{-1} consistent with terminal CO stretches. These values are indicative of weaker back-bonding from metal to CO in **2**·[PF_6] compared to **2**, consistent with a higher formal oxidation state in the former. The aforementioned [FeFe]-hydrogenase model complex has been chemically oxidized by one electron and also shows higher terminal CO stretching frequencies at 2036, 1997, and 1987 cm^{-1},[9] with shifting of the IMes ligand from an apical to a basal position. Given the *trans*-spanning nature of the phosphine arms in compound **1**, such a rearrangement is not readily accommodated and instead M–arene coordination is perturbed from μ_2:(η^3,η^3) to give a *pseudo*-square pyramidal geometry around Fe1. The neutral ene-diene assignment of the central arene challenges a formal oxidation state assignment of **2**·[PF_6] as $Fe^{I}Fe^{II}$ and underscores the potential redox participation of the central arene in the interconversion of **2** and **2**·[PF_6]. Such ambiguity in formal oxidation state assignments is not uncommon for non-innocent ligands.[11] Although the central arene may also be regarded as a formal electron acceptor and redox non-innocent ligand, its most notable aspect is the ability to accommodate a variety of coordination modes and support reversible electron-transfer chemistry at the Fe_2-(μ_2-arene) unit.

In summary, the compounds presented here show that the combination of pendant donors surrounding an arene moiety provides a versatile multidentate platform to support a variety of dinuclear complexes of first-row transition metals. Beyond the intriguing structural aspects, the redox-induced reorganization of the arene highlights its flexible coordination modes and the ability to accommodate electron transfer chemistry. Future work will focus on employing the redox non-innocence and coordination flexibility of π-bound aromatic systems for reactivity.

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